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Heterophase inclusions as a source of non-selective optical losses in high-purity chalcogenide and tellurite glasses for fiber optics

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ABSTRACT

The results of investigation of the impurity and phase inclusions as sources of non-selective losses in high-purity chalcogenide and tellurite glasses are reported. Extinction on the SiO_2 inclusions is shown to be responsible for non-selective losses in the chalcogenide glasses obtained by direct synthesis from elements in quartz equipment. Optimization of the temperature/duration conditions of the synthesis makes it possible to decrease these losses. The problem of achieving the theoretical minimum of optical loss in the glasses prone to crystallization is considered. The minimal scattering loss in such glasses can be limited not only by "freezing" fluctuations but also by the phase inhomogeneity of the glasses. A substantial contribution of the phase inclusions to optical losses is demonstrated on the example of high-purity tellurite glasses. The scattering in highly homogeneous samples of these glasses appears to be two orders of magnitude higher than the known theoretical value for scattering on "freezing" fluctuations.

1. Introduction

Active development of chalcogenide and tellurite glasses for fiber IR optics has started in 1980s–1990s. It was assumed that these materials could provide the optical losses level lower than that of the quartz glass. This was based on the theoretical estimations of the minimum intrinsic loss: $\sim 10^{-2}$–10^{-3} dB/km [1–3], which is 1–2 order of magnitude lower than the quartz glass values. However, despite the achievements of chalcogenide and tellurite glass technology appeared during last decades, the optical losses in the fibers obtained are still higher than those in quartz glass fibers. According to recent reviews [4,5] the best results reported for chalcogenide fibers are 12 dB/km at 3 μm (the As-S glass fiber) and < 50 dB/km at 3.7 μm (the As-Se glass fiber). The best record for tellurite fibers is 20 dB/km at 1.55 μm [4]. In contrast to quartz glass, the high level of homogeneous (dissolved) impurity removal did not make possible to reach the maximum transparency of these materials. The optical loss spectra of the fibers obtained from the most pure samples of chalcogenide and tellurite glasses reveal regions where the bands of selective absorption typical for homogeneous impurities are absent. At the same time, the total level of non-selective loss remains to be orders of magnitude higher than the expected intrinsic attenuation [1–3].

Non-selective losses should be associated primarily with the presence of the impurity and phase inclusions in the material. As a rule, their distinctive feature consists in non-selective character of optical losses in the whole range of the material transparency. The search for heterogeneous sources of extrinsic losses becomes, therefore, necessary for a further reduction of optical losses in high-purity chalcogenide and tellurite glasses for fiber optics.

The impurity inclusions with the refraction indices differing strongly from that of a glass represent the main source of the non-selective losses. They can provide a significant contribution to the material attenuation even at low concentrations. The main method of producing chalcogenide and tellurite glasses for fiber applications is the synthesis of glass-forming melt in the equipment made from another material. This allows one to obtain glasses with a low content of homogeneous impurities, but does not exclude contamination by the equipment material inclusions.

An important difference of chalcogenide and tellurite glasses compared to quartz glass consists in their higher tendency to phase separation (crystallization and liquid-liquid separation). The increased probability of the phase inclusion formation can provide the optimistic theoretical predictions of minimum loss in these glasses to be an unreliable reference point for their technology. Indeed, all the theoretical estimations of intrinsic scattering in chalcogenide and tellurite glasses [1–3] were based on the model of "freezing" equilibrium thermodynamic fluctuations of melt [6,7]. This model does not take into account the principal difference between the processes which occur as liquid cools down under conditions far from the phase separation points (melting or demixing temperature) and those observed on cooling down

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a glass melt passing through these points. As a result, the model contains no parameters describing different tendencies of glasses to phase separation and includes only the “fictive” temperature of equilibrium fluctuations freezing. The amplitude of such fluctuations becomes lower as temperature of the melt decreases. However, on entering the metastable region the heterogeneous fluctuations leading to the formation of new phase nuclei (phase inclusions) begin to play a significant role. As a consequence, the scattering losses γ_{sca} in the glass will arise not only from “freezing” fluctuations but also from all the phase inclusions appeared and grown as the glass-forming melt cools down: $\gamma_{sca} = \gamma_f + \gamma_p$ (where γ_f and γ_p - fluctuation and phase component of the scattering losses). This circumstance can be critical when estimating the reachable minimum of losses in the glasses showing the tendency to phase separation.

In this work a brief review is presented on the methods and main results of studies of heterophase inclusions as sources of non-selective scattering in high-purity chalcogenide and tellurite glasses.

2. Experimental methods

The high sensitivity of optical losses to the presence of inclusions in a material imposes rather strict requirements to the investigation methods. At the loss level acceptable for IR fiber optics (~100 dB/km) it is necessary to control 10 nm–10 μm inclusions with concentrations of $1–10^{12}$ cm^{-3} which corresponds to the dispersed phase volume fractions of $\sim 10^{-9}$–10^{-3}% [8]. The sensitivity of traditional methods for studying the phase inclusions in glasses (XRD, SAXS, DSC) does not allow one to control the disperse phase at such low level. The low concentration of the impurity inclusions and impossibility of studying bulk samples make the electron microscopy (EM) and scanning probe microscopy (SPM) inappropriate for the inclusion size analysis in high-purity materials. Observation of nanoscale inclusions by the optical microscopy is unavailable. The differential scattering methods, in particular 3D laser ultramicroscopy (3D LUM), represent the most efficient techniques for studying optical inhomogeneities in high-purity materials. It is also important that these methods initially provide some information on optical losses caused by heterophase inclusions.

2.1. Principles of 3D LUM. Light scattering by individual inclusions

3D LUM is intended specially for determining the concentration and size distribution of submicron impurity and phase inclusions in the bulk samples of high-purity materials for fiber - optic applications [9,10]. The method is based on the CCD registration of the laser radiation scattered by individual inclusions in the orthogonal direction to the incident beam when the sample is scanned along the microscope optical axis (Fig. 1). 0.63–0.98 μm lasers are employed. Sizes of the inclusions that can't be resolved by the microscope objective are determined from the brightness of the diffraction spot images by solution of the inverse problem of light scattering on the basis of Mie theory [11]. A set of polystyrene latex standard particles is used as size standards. The numerical concentration of inclusions is found by the single-particle count. The measurement of the light scattered by inclusions at a varied probe beam wavelength and polarization and at a varied scattered light collection angle makes it possible in some cases to determine the inclusion refractive indices. 3D LUM can be used to control inclusions in the materials transparent not only in the visible but also in the near IR region.

The method is characterized by a low size detection limit ($\sim n \times 10$ nm) and a wide range of the detectable concentrations ($1–10^9$ cm^{-3}), 3D LUM can scan a sample up to a few centimeters depth. The data on concentrations, sizes and refractive indices of inclusions are used to estimate their contribution to the optical losses in the whole transparency range of the material studied.

2.2. Integral light scattering by ensemble of inhomogeneities

Impurity inclusion concentrations in high-purity materials are, as a rule, substantially lower than those 3D LUM is able to determine ($n_{max} \sim 10^9$–10^{10} cm^{-3}). This does not necessarily occur with phase inclusions. At the concentrations of scattering centers above n_{max} the measurements of integral scattering (by ensemble of such centers) become desirable which can be easily carried out with LUM setup. It would be sufficient to decrease apertures, lens magnifications and CCD resolution so that each pixel of the laser beam image corresponds to the signals coming from all the scattering centers within some scattering volume of the sample.

The Rayleigh ratio R_{90}, describing the scattering loss into infinitely small solid angle θ in the 90° direction [7], is measured when comparing brightness E of identical patterns of the laser beam image in the studied and standard (benzene or quartz glass) samples. The use of various combinations of polarizers of probing and scattered radiation provides possibilities of finding depolarizations of the scattered radiation at the unpolarized $\Delta_U = E_{UH}/E_{UV}$, polarized orthogonal $\Delta_V = E_{VH}/E_{VV}$ and parallel $\Delta_H = E_{HH}/E_{HV}$ to the scattering plane probing beam, as well as the value of cross-polarization $\Delta_X = E_{HV}/E_{UU}$ (the first and the second index corresponds to the probing and scattered radiation, respectively). The measurements made in accordance with the known scheme [11] make it possible in some cases to determine the scattering matrix type.

3. Results and discussion

3.1. Dispersion analysis of impurity inclusions in chalcogenide glasses

The role of impurity inclusions is clearly demonstrated by the results of the investigation of the equipment material contamination effects in the process of synthesis of chalcogenide glasses for fiber

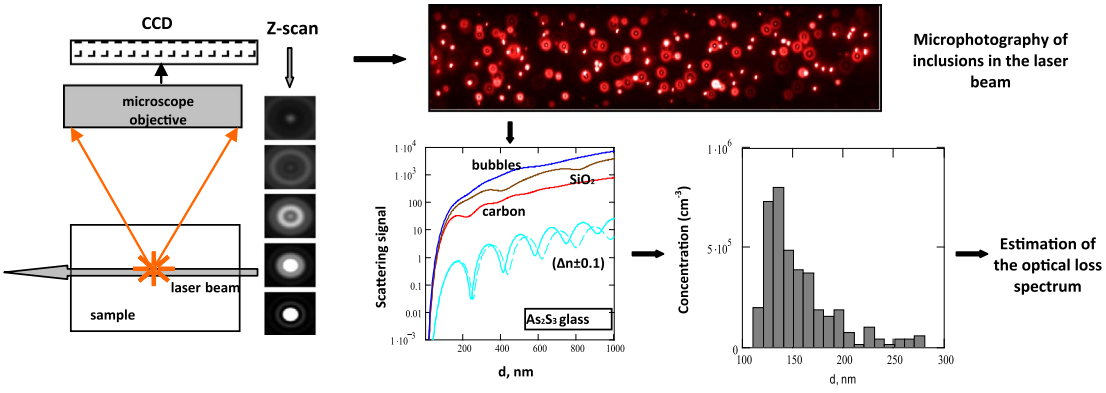

Fig. 1. 3D LUM technique and analysis procedure.